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13. ABSTRACT (Maximum 200 words)

Experimental verification of enhanced passive mechanical damping as derived from ferroelectric-embedded particulates within a metal matrix composite has been demonstrated. Specifically, experimental results indicate relatively high damping is exhibited by composites containing a discontinuous dispersion of ferroelectric (tetragonal) $BaTiO_3$ particulate; damping capability is reduced as temperature increases and a transformation to a cubic form occurs. Experiments performed at the Los Alamos Neutron Science Center (LANSCe) indicate that the mechanism of damping is associated with ferroelectric domain rotation that occurs in response to external stress. Early results additionally indicated that the stability of tetragonal form of $BaTiO_3$ is very sensitive to a variety of processing-related factors serve to limit the processing options available to synthesize the composite. Processing studies that examined the influence of ferroelectric particle size, interfacial strength, and composite processing methodology were performed. Overall, results indicate a potential for effective multifunctional (strengthening plus damping) behavior by ferroelectric reinforcement strategies provided that the tetragonal form of the particulate can be maintained through processing. Further, the mechanisms of enhanced damping and strengthening should be directly extendable to reinforcement by shape memory alloys (SMA), since both involve energy absorption by the activation of certain crystallographic translations.

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Structural Piezoelectric Single Crystal Array Networks (Structural P-SCAN)

Final Report

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Submitted to

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Executive Summary

Structural Piezoelectric Single Crystal Array Networks (Structural P-SCAN)

Project Objectives and Chronological Overview

The broad objective of the proposed program was to create a structurally-capable metal matrix composite, with the reinforcement being additionally capable of piezoelectric (mechano-electrical) behavior. It is speculated that, if successful, the reinforcement would thus serve a multifunctional role by imparting both strength and an enhanced ability to dampen mechanical or acoustic vibrations when imparted to a structural system. Illustrations of the notional concept have been included in the Interim Progress reports submitted previously.

The initial approach to the project (circa 2001) involved the use of solvent-mediated reaction synthesis (SMRS) as a means to create an in-situ derived, piezoelectric-capable reinforcement within the metal matrix. This approach complemented the Principal Investigator's previous research efforts in this area, but extended it to include more complex reinforcement compositions, e.g., multi-cationic oxides. The thesis work of Jennifer Franklin established that the SMRS approach was indeed capable of producing a variety of appropriate reinforcement compositions within a variety of target matrices. Zinc Oxide (ZnO), barium titanate ($BaTiO_3$), and lead titanate ($PbTiO_3$) of a variety of nominal volume percentages were synthesized within copper and/or iron matrices. In the case of $PbTiO_3$, the synthesis reaction was conducted within a high energy ball mill in order to avoid the need to thermally-activate the reaction. While successful from a chemical point of view, however, the resulting composite microstructures were extremely complex in terms of their morphology, making their subsequent characterization difficult. Further, in the case of $BaTiO_3$, the non-equilibrium cubic (non-piezoelectric) crystal structure formed in the as-synthesized state; attempts to transform to the necessary tetragonal structure proved unsuccessful. A copy of Ms. Franklin's thesis is accessible electronically via the URL provided in the Bibliography section of this report.

Concurrent with the efforts of Jennifer Franklin, graduate student Adam Goff developed a predictive model that served to quantify the potential damping effects if governed by a "joule-heating" mechanism of energy dissipation. In this work, Goff utilized an Eshelby Inclusion approach to predict the influence of an imposed mechanical or acoustical excitation stimulus on the piezoelectric tensor of a variety of embedded, potentially electrically-active reinforcements within several candidate metallic matrices. The model predicted that a relatively large intrinsic piezoelectric response coupled with a highly conductive metallic matrix translated into large quantities of joule heating – and thus, maximum damping capabilities.

Goff's work also included an experimental component – that is, he fabricated a $BaTiO_3$-reinforced nickel matrix composite utilizing high energy ball milling (mechanical alloying) as a blending and homogenization technique and densified using hot isostatic pressing (HIP). Unfortunately, x-ray diffraction of the final composite indicated that the $BaTiO_3$ was not present in the desired or necessary tetragonal form, and thus did not exhibit enhanced damping characteristics. Heat treatments attempted to transform the $BaTiO_3$ to the equilibrium tetragonal structure were unsuccessful. Subsequent investigations revealed that the stability of the equilibrium tetragonal phase in $BaTiO_3$ is compromised by high temperatures, such as that associated with necessary processing conditions required to consolidate, and by small particle sizes. That is, in the latter regard, as the tetragonality of the $BaTiO_3$ decreases as the size of the particle (reinforcement diameter) decreases. While this non-intuitive, extrinsic (size-related) effect was not expected, it was nonetheless subsequently confirmed through investigations available in the literature.

Follow-on thesis investigations by Ben Poquette and Ted Asare provided huge advancements, both in terms of the demonstration of concept and in our understanding of the mechanisms active in the composites. Ted Asare investigated the effect of particle size on the tetragonality of the $BaTiO_3$ reinforcement, and successfully fabricated a series of copper matrix composites of varying reinforcement sizes. His work demonstrated that damping capability was linked to reinforcement particle size, thereby confirming the intrinsic influence of the effect. Damping capability was measured as a function of temperature, thus enabling the use of a discontinuity at the 130°C tetragonal to cubic phase transition as definitive evidence of a positive effect of the piezoelectric-capable phase on damping behavior. The work of Asare also served to clarify the probable mechanism of damping improvement from that associated with piezoelectric behavior to behavior associated with domain movement in the $BaTiO_3$. In the former regard, piezoelectric effects rely on the presence of a poled crystal – a feature not present or possible in the random and discontinuously-reinforced composites fabricated. Thus, consistent with our present understanding, these composites are now referred to as ferroelectric-reinforced (FR) composites, and provide enhanced damping characteristics as a consequence of domain movement that occurs in response to an imposed stress.

Ben Poquette investigated the influence of the relative volume percentage of $BaTiO_3$ in bronze-matrix composite variants. Consistent with the work of Asare, the composites exhibited increased damping character as the volume percent of $BaTiO_3$ increased. Poquette also demonstrated the successful electroless plating of copper onto the surface of the $BaTiO_3$ particles, performed to improve the interfacial characteristics of the composite when incorporated into the bronze matrix.

Near the conclusion of the present contract, a series of neutron diffraction experiments were conducted at the Los Alamos Nuetron Science Center (LANSCe). These experiments confirmed the mechanism of damping improvement speculated by results of efforts to date. The following is a summary of those experiments, and a synopsis of our current understanding of these composites as revealed by the research conducted in this program.

Our Current Understanding and Successful Proof of Concept

Our experiments on bronze (Cu-Sn)-$BaTiO_3$ particulate-reinforced MMCs demonstrate that the presence of the ferroelectric ceramic contributes to the damping properties of the composite at temperatures below the Curie temperature of the ceramic[1]. Figure 1 is a plot of the damping capacity (tan delta) as a function of temperature for the Cu-Sn matrix, bulk $BaTiO_3$, and composites with 30 and 50 volume percent $BaTiO_3$. Below the Curie temperature, damping in the composites is due to three mechanisms: ferroelastic-damping from the reinforcement, composite-damping due to interfacial interactions, and matrix twinning. Above the Curie temperature, only the latter two mechanisms contribute to damping in the composites. A distinct decrease in the damping capacity of the bulk $BaTiO_3$ and the composites is observed at the Curie temperature; thus, we conclude that the ferroelastic character of $BaTiO_3$ contributes to the damping properties of the MMC below the Curie temperature of the ferroelectric. Ferroelastic damping results from the stress-induced twinning of the ferroelectric domains during cyclic loading; reorientation of the domains occurs by formation of 90^o twins. It is logical to assume that stress transfer from the Cu-Sn matrix to the $BaTiO_3$ reinforcement leads to twin formation in the reinforcement.

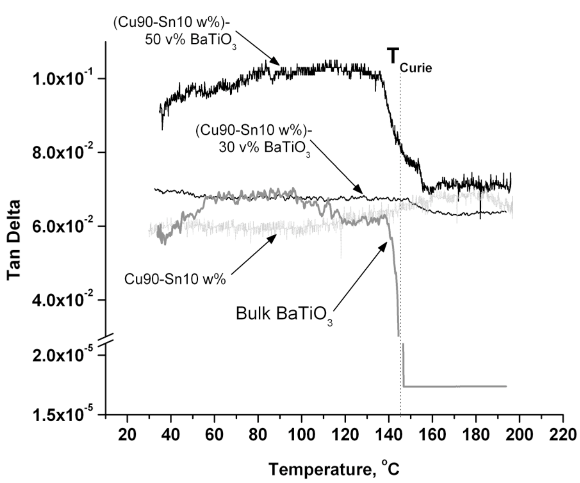

Figure 1: Tan delta as a function of temperature for ferroelectric reinforced MMCs and individual composite constituents.

Characterization of multifunctional composite materials is often hindered by the lack of in situ characterization methods for investigating some or all of the multifunctional properties of the material due to shielding of embedded reinforcement by the matrix. Specifically, in the case of the ferroelectric reinforced metal matrix composites investigated in this program, the metal matrix physically and electrically shields the ferroelectric particles, thus prohibiting direct electrical and dimensional observations as a means of quantifying domain motion under an applied load. However, the SMARTS instrument at the Los Alamos Neutron Science Center has the unique capability of measuring lattice strain, by neutron diffraction, in the matrix and reinforcement simultaneously under applied load in two orthogonal

[1] US Patent Pending: Piezoelectric Ceramic-Reinforced Metal Matrix Composites. S. L. Kampe, J. P. Schultz, A. O. Aning, A. Goff, and J. Franklin.

directions. Figure 2 is a schematic of the SMARTS instrument. The horizontal load frame is oriented such that the loading is axis 45º from the incident neutron beam and detector banks are located on both sided of the load frame. The orientation of the load frame and location of the detector banks with respect to the incident beam are such that crystallographic planes which diffract into detector bank 1 have lattice plane normals perpendicular to the loading direction and crystallographic planes which diffract into detector bank 2 have lattice plane normals parallel to the loading direction, as shown in Figure 3.

A schematic of a tetragonal unit cell is also shown in Figure 3; the orientation of the unit cell as shown will have diffraction of (002) planes into bank 1 and (200) planes into bank 2. If the unit cell was rotated +/-90º in the plane of the page, as would occur in twinning, then the banks into which the planes diffract would switch because of the 90º rotation of the planes normals. Thus, changes in the ratio of peak intensities of the (200) and (002) planes in a single bank are indicative of twinning.

The unique capabilities of observing the strain in both the matrix and reinforcement simultaneously and observing the changes in the domain orientation due to twinning under an applied load afforded by SMARTS provides a means of directly quantifying the mechanical response of the $BaTiO_3$ particles in the metal matrix. The primary objective of our SMARTS experiments was to demonstrate that reversible twinning occurs in the $BaTiO_3$ under cyclic loading.

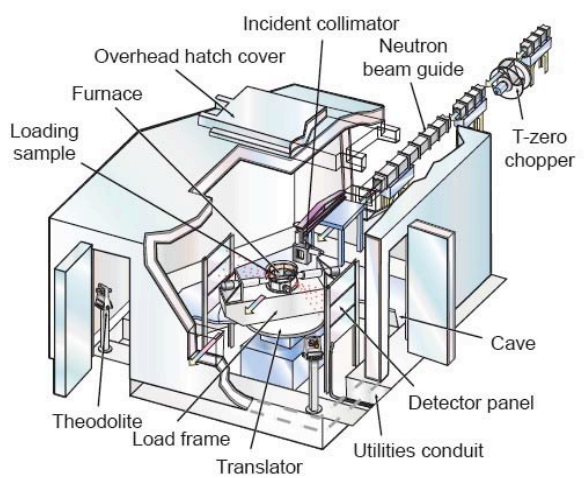

Figure 2: Schematic of SMARTS instrument.

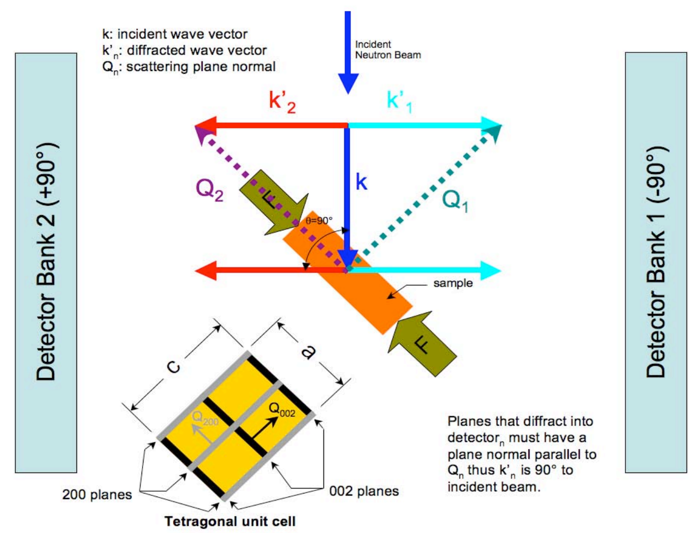

Figure 3: Schematic of SMARTS diffraction orientations.

Experimental Details and Results

To confirm that stress transfer from the matrix to the reinforcement leads to twinning in the reinforcement, in situ neutron diffraction patterns were collected during cyclic compression loading on a (Cu-Sn)-$BaTiO_3$ 30vol% sample. The form of the cyclic compressive loading was sinusoidal, an amplitude of 10 MPa superimposed on a constant compressive stress of 30 MPa; neutron diffraction patterns were collected for cycles 1, 2, 5, 10, 25, and 50. Figure 2 shows the normalized peak intensities for the (002) and (200) planes as a function of the macroscopic stress state of the composite for cycles 5, 10, 25, and 50. Peak intensities were determined from single peak fits to neutron diffraction patterns from the +90º detector bank of the SMARTS instrument. In a tetragonal system such as $BaTiO_3$, changes in the ratio of the (002) and (200) peak intensities with applied stress are a direct observation of deformation twinning. Figure 2 shows that as the magnitude of the macroscopic compressive load increases the number of (002) planes satisfying the Bragg condition decreases and the number of (200) planes meeting the Bragg condition increases; upon unloading the intensities in the two peaks return to their initial values. Over the applied stress range of -20 to -40 MPa, increasing the compressive load results in the formation of deformation twins with (002) lattice-plane-normal preferentially oriented perpendicular to the loading direction and as the compressive load is removed detwinning occurs. A linear least squares fit of the intensity as a function of stress is also shown on the figure for both planes. The slope of the lines is proportional to number of domains with a plane normal oriented such that Bragg condition is met. The slope of the (200) line is half the (002) because there are twice as many (200) planes as (002) planes and the absolute intensity changes for the (200) and (002) planes are equal, thus when the intensity is normalized slopes are different by a factor of 1/2. We conclude that the observed twinning/detwinning that occurs during cyclic loading, as observed by in situ neutron diffraction, is mechanism which leads to enhanced damping in ferroelectric reinforced MMCs below the Curie temperature.

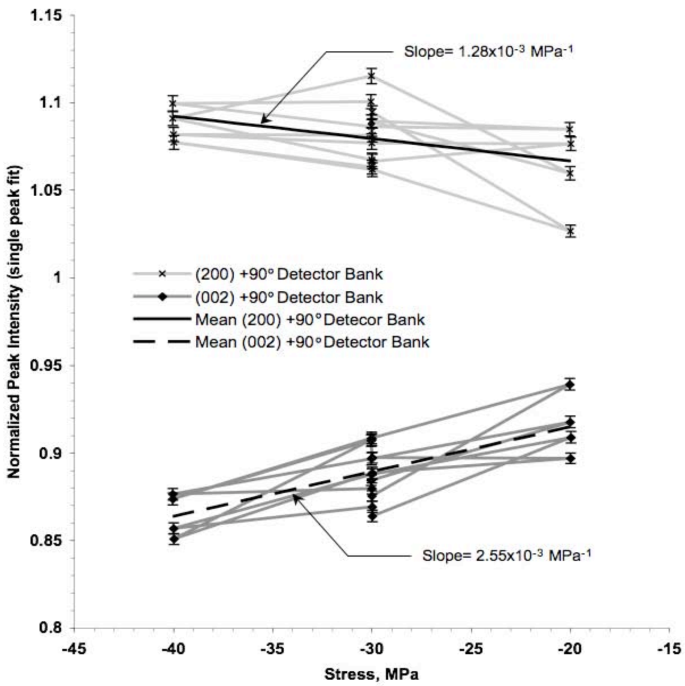

Figure 4: Normalized peak intensity for $BaTiO_3$ (200) and (002) planes from in situ neutron diffraction during cyclic loading of ferroelectric reinforced MMC at 25°C, cycles 5, 10, 25, and 50 shown.

Future Directions and Opportunities

As our program moves past the proof of concept phase, the primary goals are to demonstrate MMCs that have practical significance and simulate applications that maximize the potential of the microstructurally active reinforcements to dissipate energy. Thus, we have initiated fabrication and testing composites with Ni matrices. Also, we have identified structural components such as axles and other a cantilevered rotating member as prime applications for microstructurally active MMCs because any point in the part is cycled through repetitive tension/compression which maximizes the energy dissipation of the microstructurally active reinforcement. Additionally, we are extending our work to include other microstructurally active reinforcements such as shape-memory alloys (SMAs) which have been show to have significant damping ability due to pseudoelastic deformation behavior[2]. In-situ neutron diffraction will continue to play a key roll in forming and validating our understanding of the microstructural phenomena that impart macroscopic multifunctionality to our MMC systems.

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